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Full Length Article

Studies on phosphorescence and trapping effects of Mn-doped and undoped zinc germinates

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ABSTRACT

Photoluminescence and phosphorescence from different recombining centers in the Mn^{2+}-doped and undoped Zn_2GeO_4 phosphors have been observed. By UV excitation the undoped sample presents a broad band of blue–white emission from the host defects while the Mn-doped samples show both the host and Mn^{2+} emissions with different phosphorescent durations. At the beginning of UV excitation after the phosphorescence has been exhausted, the fluorescent time dependence of Mn^{2+} exhibits a fast decay process to a constant intensity, different from the rising or charging process as the typical behavior for the common persistent phosphors. This unusual behavior was studied using electron paramagnetic resonance (EPR) spectroscopy. A decrease of the EPR signal from Mn^{2+} was found for the sample under UV irradiation, suggesting the occurrence of ionization of Mn^{2+} to Mn^{3+}. A slow recovering process of the ionization has also been detected, which is consistent with the observation of phosphorescence from Mn^{2+} doped samples.

1. Introduction

In recent years, persistent phosphors have been studied by many investigators in the effort to develop the phosphors with colorful emissions [1] for more applications, e.g., in vivo biomedical imaging [2,3]. The phosphorescence examination is also an effective way to analyze the charge transfer among the trapping defects [1]. Optical charging process in phosphorescence may provide important facts that reveal the trapping mechanism. In our previous work [4], we have observed a slowly rising time dependence of the photoluminescence of $SrAl_2O_4$:Eu,Dy during the excitation period, which was attributed to a trap charging process.

The zinc germinate, Zn_2GeO_4, in nanoscale has been reported having good photonic and electronic characteristics as the photoanode to increase the open circuit voltage of CdSe solar cell [5], anodes for Li-ion batteries to improvement the capacity and cycling life [6], as well as for the UV detector with fast response [7]. The luminescent properties of undoped and Mn^{2+} doped Zn_2GeO_4 have been studied in several reports [8–12], and the host without doping also showed a bluish emission from its native defects by UV excitation [5]. In this work, photoluminescence and phosphorescence of Mn^{2+} doped and undoped Zn_2GeO_4 have been investigated in details for better understanding the electron/hole trapping mechanism. Phosphorescence from both the Mn^{2+} ions and host defects in Zn_2GeO_4 has been observed upon UV excitation, while the Mn^{2+} ions present a longer phosphorescent duration than the defects. The charging process has also been studied and different behaviors of Mn^{2+} and defects observed. The electron paramagnetic resonance (EPR) signal of Mn^{2+} has been found being decreased during the UV irradiation, indicating that the population of Mn^{2+} ions decreases in the trapping state and the valence changes from Mn^{2+} to Mn^{3+}. A slow recovering process of the ionization has also been detected, which is consistent with the decay observation of phosphorescence from Mn^{2+} doped samples.

2. Experimental

2.1. Samples preparation

All samples were prepared by mixing the row materials (4N in purity) of ZnO, GeO_2, and $MnCO_3$ according to the desired ratio sintered at 900 °C in N_2+H_2 (8%) reduced atmosphere for 2 h, while both the heating-up and cooling-down processes took 4 h. The Mn doping concentrations are 0 (undoped), 0.001, 0.004, and 0.02 (in mol ratio x, the formula is $Zn_{2-x}Mn_xGeO_4$), respectively.

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2.2. Measurements

IThe measurements of photoluminescence emission, excitation, and phosphorescence spectra were performed using a SPEX Fluoro Max III and Horiba FluoroLog Spectrometers. The phosphorescent emission spectra were collected by averaging the data acquired by forward and reverse wavelength scan to eliminate the influence of the phosphorescent decay. The timing offset could be several seconds after manually blocking the excitation beam but would not significantly affect the relative line shape of the spectra. The EPR spectra were measured using a Bruker EMXplus X-band spectrometer. Photo-stimulated EPR was performed by illuminating (254 nm) the sample through the optical window of microwave chamber. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Photoluminescence spectra

Upon the UV excitation at 260 nm, the updoped Zn_2GeO_4 sample presents a blue–white emission of the broad band extends from the near-UV to orange–red region (Fig. 1, dashed line), arising from the host crystal defects, which were identified by the EPR experiments as $V_O^{\bullet}$ or $Zn_i^{\bullet}$ for the donor and V_{GE} or $V_{Zn}^{\bullet}$ the acceptor in Kröger–Vink notations [8]. The photoluminescence of the Mn^{2+} doped sample exhibits a green emission within the $3d^5$ configuration ($^4T_1 \rightarrow {}^6A_1$) of Mn^{2+} accompanied by the host emission (Fig. 1, solid line). The peak wavelength of the blue–white emission from the host defects shows a little different from that previously reported [8,9], due to the condition dependence of the defect properties on the sample preparation. The intensities of the two emission spectra in Fig. 1 are not in the same scale. Under the same measurement condition, the integrated emission intensity of the undoped sample is calculated to be one order of magnitude lower than that of the doped sample.

The low efficiency of the host luminescence can be ascribed to the strong phonon coupling of the transition with the host lattices [13], resulting in the occurrence of nonradiative process. Its broad emission band extended from ~380 nm to ~600 nm also indicates such a strong electron–phonon coupling in the radiative transition. In general the host luminescence is not as efficient as that of the properly doped activators. Nevertheless it provides an optical approach to examine the intrinsic properties of the host defects for comparison with the doped activators.

The excitation spectrum of Zn_2GeO_4:Mn^{2+} shows two bands with the peak wavelengths at ~260 nm and ~295 nm, respectively, while the undoped sample only presents a strong excitation band around 260 nm, as shown in Fig. 2. The bandgap of Zn_2GeO_4 was reported at values of 4.5 eV [5] to 4.68 eV [7] corresponding to the light wavelength around 270 nm, where in Ref. [7] the photocurrent was detected upon 254 nm UV excitation but not 365 nm. The 260 nm excitation band is due to the interband absorption of the host lattice and the one at 295 nm was attributed to charge transfer transition [9]. Mn^{2+} can be selectively excited at a longer wavelength, e.g., 330 nm, to avoid the interband absorption, yielding a single green band of Mn^{2+} emission.

3.2. Phosphorescent properties

After the UV excitation, both the Mn^{2+}-doped and undoped samples show the long-lasting phosphorescence with the same emission band shapes and positions as the photoluminescence (peaked at ~455 and ~533 nm). There were several investigators who reported that the lasting time of Zn_2GeO_4:Mn^{2+} varied from several tens of seconds to more than 1 h [11,12] since its luminescent property is strongly dependent on the preparation conditions including the undoped samples [8,9]. For the doped sample Zn_2GeO_4:0.004Mn^{2+} the phosphorescent emission from Mn^{2+} is also dominant over that from the host. To have a clear comparison of their change with time, the samples doped with different Mn concentrations have also been examined. As the Mn concentration increases, the blue–white host emission decreases dramatically. The host emission is hard to be detected at 0.02 mol ratio and almost all the emission shifts to the green band of Mn^{2+}. Fig. 3 compares the phosphorescent spectra of the samples doped with 0.001 and 0.004 of Mn^{2+} in mol ratio at different time after excitation.

For the photoluminescence, the two excitation bands peaked at 295 nm and 260 nm have the same scale of efficiencies. But for phosphorescence, only the 260 nm interband absorption is efficient in producing the afterglow. For excitation at the longer wavelength region above 300 nm, the charge transfer transition corresponding to the excitation at longer wavelength region above 300 nm takes place with the electrons transferring among the localized ions. These electrons do not ionize the trapping process and therefore do not yield phosphorescent emission, referring to the photocurrent behavior under 254 and 365 nm excitations [7].

For the sample with low doping concentration Zn_2GeO_4:0.001Mn^{2+}, phosphorescence from the host defects has the same scale as that of the Mn^{2+} ions (Fig. 3a) but decreases significantly in the sample Zn_2GeO_4:0.004Mn^{2+} doped with a higher concentration (Fig. 3b). Moreover, considering their large intensity difference of photoluminescence under the interband excitation as shown in Fig. 1, it is evident that the Mn^{2+} ions are much more competitive in capturing the electrons/holes as the radiative recombination centers. Fig. 4 depicts the phosphorescent decay processes for the doped and undoped samples with their initial intensity normalized, lasting 3 h and 1 h, respectively.

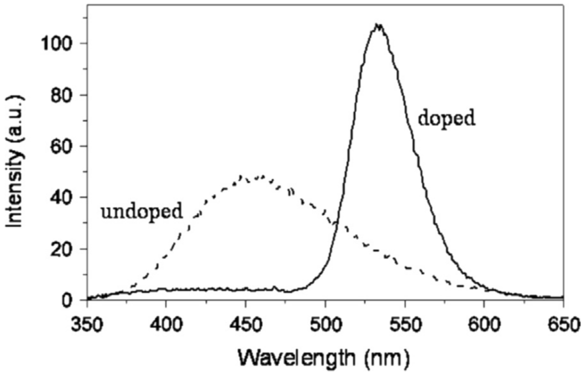

Fig. 1. Photoluminescence spectra of Mn^{2+} doped (0.4%, solid line) and undoped (dashed line) Zn_2GeO_4, excited at 254 nm.

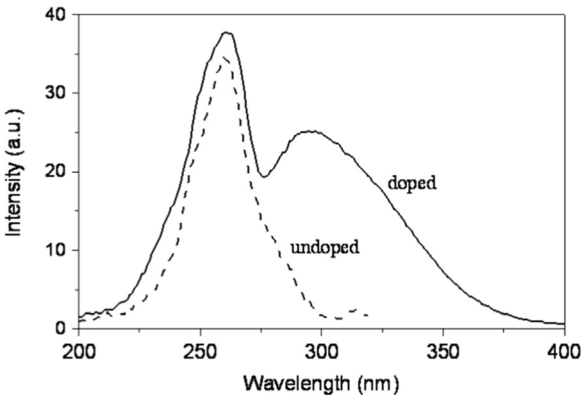

Fig. 2. Excitation spectra of the Mn^{2+} doped (0.4%, solid line) and undoped (dashed line) Zn_2GeO_4, monitored at 530 and 455 nm, respectively.

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